

# PATENT SPECIFICATION

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(21) Application No. 43854/70 (22) Filed 14 Sept. 1970  
(23) Complete Specification filed 14 Sept. 1971  
(44) Complete Specification published 24 July 1974  
(51) International Classification C02B 1/18//1/12  
(52) Index at acceptance  
C1C 20X 254 404 424 425 426  
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## (54) PURIFICATION PROCESS

(71) We, THE BRITISH OXYGEN COMPANY LIMITED, a British Company of Hammersmith House, London, W6 9DX, England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a process for the purification of water.

One known method of purifying water is to introduce a hydrate-forming gas such as propane into the water, to cool the water 15 and to raise the pressure until solid hydrate is formed, to separate the solid hydrate from the impure residue and to recover water from the hydrate by allowing the temperature and pressure to return to 20 ambient. The invention relates to a similar process using a particular and advantageous combination of hydrate-forming materials.

According to the invention there is provided a process for treating impure water 25 which includes introducing a hydrate-forming substance and a hydrate-forming aid into the water under conditions of temperature and pressure in which a solid hydrate is formed and separating the solid 30 hydrate from the impure residue, wherein the hydrate-forming substance is trichlorofluoromethane, 3-bromopropene or a mixture thereof, is employed in an amount within the range 4.0 to 8.0 mol % of the 35 amount of impure water and is introduced in the liquid state into the water and the hydrate-forming aid is a gas or liquid and is employed in an amount of at least 20 mol % of the amount of hydrate-forming 40 substance.

Formation of the solid hydrate requires particular combinations of temperature and pressure. For example for a water temperature of 15°C an elevated pressure of the 45 order of 15 bars is required whereas a water

temperature of 20°C requires a pressure of about 85 bars. At a temperature below about 8°C the pressure can be as low as 1 bar.

The solid hydrate molecule is believed to 50 have a cage-like structure of water molecules enclosing a molecule of hydrate-forming substance. We have now found that, in combination with the particular hydrate-forming substances of the invention, 55 a hydrate-forming aid having molecules of such a size that a molecule of hydrate-forming aid is also enclosed within the cage-like structure gives a hydrate of improved stability. Examples of suitable hydrate-forming aids are carbon dioxide, sulphur dioxide, hydrogen sulphide, argon and diatomic gases such as nitrogen and oxygen. Nitrogen, oxygen and carbon dioxide and 60 mixtures thereof, in being acceptable impurities in water for most purposes, are generally preferred. Air is accordingly a particularly convenient mixture for use as the hydrate-forming aid.

In general it is preferred to take the water 70 at its ambient temperature and to provide the appropriate increased pressure rather than to cool the water in order to form the solid hydrate. The process of the invention can, however, include a water cooling 75 step prior to or instead of increasing the pressure. It may also be found advantageous to cool the mixture of water, hydrate-forming substance and hydrate-forming aid during and/or after compression in order 80 to remove the heat caused by the compression. This cooling can be effected in a heat exchanger cooled by water at ambient temperature. Both the hydrate-forming substances of the present invention are liquids 85 at the ambient temperature of naturally occurring water, ie within the range of 0 to 30°C, and give a hydrate which can be formed at such temperatures. Whether or not the hydrate-forming aid is in the liquid 90

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state on introduction into the water depends upon the pressure at which the hydrate-forming aid is introduced.

The amount of hydrate-forming substance 5 is preferably within the range 5.5 to 6.7 mol percent of the amount of impure water. The amount of hydrate-forming aid is preferably within the range 90 to 120 mol percent of the amount of hydrate-forming 10 substance.

Separation of the solid hydrate from the impure residue can conveniently be effected by filtration. The solid hydrate is then preferably washed with purified water which 15 can if desired be water that has been purified by a process according to the invention.

A volume of washing water within the range of 5 to 10% of the volume of hydrate 20 has been found to give a satisfactory degree of washing.

After separation, and after any washing, purified water can be recovered from the solid hydrate by reducing the pressure or 25 increasing the temperature to the level at which the hydrate decomposes.

In the form of the process using elevated pressure to form the solid hydrate, it is preferred to conduct the separation at or 30 just below the pressure at which the decomposition would occur. In this way the energy consumption is kept to a minimum.

On decomposition, a layer of purified water, a lower layer of liquid hydrate- 35 forming substance and, if it is in the vapour state at the decomposition temperature and pressure, an upper layer of hydrate-forming aid are obtained and can be readily separated from each other. The hydrate- 40 forming substance and hydrate-forming aid are preferably collected for re-use.

If the separated water contains undesirably large amounts of hydrate-forming substance or hydrate-forming aid these should 45 be reduced by a standard water purification treatment. This is particularly likely if the hydrate-forming aid is a liquid at the decomposition temperature and pressure. By using the preferred form of the process such 50 further treatment is generally not required, the amount of hydrate-forming substance in the separated water being sufficiently small to be acceptable for most required end uses for the water. Similarly the preferred 55 hydrate-forming aids are, as specified above, generally tolerable in the water.

The process of the invention is advantageous in using hydrate-forming substances that are liquid at the ambient temperature 60 of naturally occurring water and that can form a hydrate at such temperatures. The formation of a hydrate at the ambient temperature of the water enables cooling to be avoided. Since they are in the liquid 65 state, the amount of energy required for

the compression, even if the hydrate-forming aid is a gas, is considerably less than would be required to compress a hydrate-forming gas such as propane to the required level. This represents a considerable saving in the energy consumed to operate the process and offers the further advantage that the process can be operated mainly by pumps rather than by compressors. 70

The invention is described below by way of example with reference to the accompanying figures in which

Figure 1 is a diagrammatic view of apparatus for carrying out the process in 80 a batchwise manner, and

Figure 2 is a diagrammatic flow sheet showing how the process can be conducted in a continuous manner.

The apparatus shown in Figure 1 includes 85 a reaction tank, indicated generally by the reference numeral 10, having a lower conical portion 12 and having a conduit 14 which can act as an inlet for impure water, an inlet 16 for the hydrate-forming 90 substance, a pressure release outlet 18, and a purified water outlet 20. The vessel 10 is also provided with a stirrer 30 and a filter plate 32. The conduit 14 is supplied by an inlet pipe 22 having a valve 26 and 95 leading from a pump 24. The inlet 22 also provides the inlet for the hydrate-forming aid. A valved outlet 28 for removing from the tank firstly the impure residue and secondly the re-formed hydrate-forming 100 substance is also connected to the conduit 14. A conduit 36 leads from the purified water outlet 20 to a storage tank 38 and then through a valve 40 to a spray header 42. The removal point for the purified water 105 is provided by a valved outlet 34.

In operation, a hydrate-forming substance is introduced into the vessel 10 through inlet 16. Impure water is then introduced into the vessel 10 through inlet 22 and 110 conduit 14. The hydrate-forming aid is then introduced through inlet 22 and conduit 14, the required elevated pressure in the vessel being created by the pumping in of the impure water and of the hydrate-forming aid. The materials in the vessel 10 are stirred by the stirrer 30 until the hydrate-forming process is complete. This can be detected by the stirrer's slowing down on formation of the solid hydrate. The valved outlet 28 and the valved inlet 40 are then opened, allowing the escape through outlet 28 of impure residual water and its replacement by purified water prepared in a previous cycle and stored in the tank 38. The 125 spray header 42 should desirably be of a shape and construction to create a substantially horizontal interface between the purified water introduced and the impure residual water. The stirrer 30 should not be 130

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used during this operation.

Introduction of purified water can stop when the pure/impure water interface reaches the filter plate 32. At this stage 5 the vessel 10 contains solid hydrate supported by filter plate 32 and purified water introduced from tank 38. The valves 28 and 40 are then closed and the valve 34 opened. The pressure in the vessel 10 forces 10 purified water out of the outlet 20 and the reduction of pressure resulting from its release allows the solid hydrate to melt giving purified water, free hydrate-forming substance and free hydrate-forming aid. The 15 hydrate-forming substance is withdrawn through the conduit 14 and valve 28. Hydrate-forming aid, if obtained in the gaseous state, can be withdrawn through the pressure release valve 18. A part of the 20 product water is returned through the conduit 36 to the tank 38.

In the continuous form of process shown in Figure 2 impure water is pumped into a reactor 50 through a line 52 and the 25 hydrate-forming substance is pumped into the reactor 50 through a line 54. The hydrate-forming aid is pumped into the reactor through a line 56.

The reactor 50 is maintained at a pressure 30 sufficiently high to cause formation of solid hydrate and accordingly the introduction of the three materials immediately results in some formation of solid hydrate. A slurry of solid hydrate is continuously 35 withdrawn through line 58, passed through an air-cooled filter 60 from which impurity-rich water is withdrawn by line 62 and can be either discarded or recycled for further treatment. A slurry of increased solids content 40 is withdrawn through line 64 and washed in a washer 66. Impure water is withdrawn through line 68 and can be discarded or recycled for further treatment.

The solid hydrate is passed through an 45 expansion valve 70 into a decomposition vessel 72. Line 54 returns from vessel 72 to the reactor 50 to return the hydrate-forming substance for re-use. Purified water is withdrawn through line 74, a part being 50 recycled through a conduit 78 to washer 66 to wash the incoming slurry. Gaseous hydrate-forming aid returns through line 56 to the reactor 50. In the interests of clarity the figure does not show the pumps required 55 for these various steps, nor the arrangements for replenishing the amounts of hydrate-forming substance and hydrate-forming aid on recycling.

**WHAT WE CLAIM IS:—**

60 1. A process for treating impure water which includes introducing a hydrate-

forming substance and a hydrate-forming aid into the water under conditions of temperature and pressure in which a solid hydrate is formed and separating the solid 65 hydrate from the impure residue, wherein the hydrate-forming substance is trichlorofluoromethane, 3-bromopropene or a mixture thereof, is employed in an amount within the range 4.0 to 8.0 mol % of the 70 amount of impure water and is introduced in the liquid state into the water and the hydrate-forming aid is a gas or liquid and is employed in an amount of at least 20 mol % of the amount of hydrate-forming 75 substance.

2. A process as claimed in claim 1, wherein elevated pressure is employed in the formation of the solid hydrate.

3. A process as claimed in claim 1, or 80 claim 2, wherein the hydrate-forming aid is one or more of carbon dioxide, sulphur dioxide, hydrogen sulphide, argon, nitrogen and oxygen.

4. A process as claimed in claim 2, 85 wherein the hydrate-forming aid is air.

5. A process as claimed in any preceding claim, including a water cooling step.

6. A process as claimed in any preceding claim, wherein the amount of hydrate- 90 forming substance is within the range 5.5 to 6.7 mol percent of the amount of impure water.

7. A process as claimed in any preceding claim, wherein the amount of hydrate- 95 forming aid is within the range 90 to 120 mol percent of the amount of hydrate-forming substance.

8. A process as claimed in any preceding claim, wherein the solid hydrate is separated 100 from the impure residue by filtration.

9. A process as claimed in claim 8, wherein the separated solid hydrate is 105 washed with purified water.

10. A process as claimed in claim 8 or 105 claim 9, wherein elevated pressure is used to form the solid hydrate and a pressure just below that at which decomposition of the solid hydrate would occur is used for the separation. 110

11. A process as claimed in any preceding claim, wherein purified water is recovered from the solid hydrate by reducing the pressure or increasing the temperature to the level at which the hydrate decomposes. 115

12. A process as claimed in claim 1, substantially as described herein with reference to the drawings.

For the Applicants  
PETER JACKSON  
Chartered Patent Agent

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2 SHEETS  
*This drawing is a reproduction of  
the Original on a reduced scale.*  
SHEET 1

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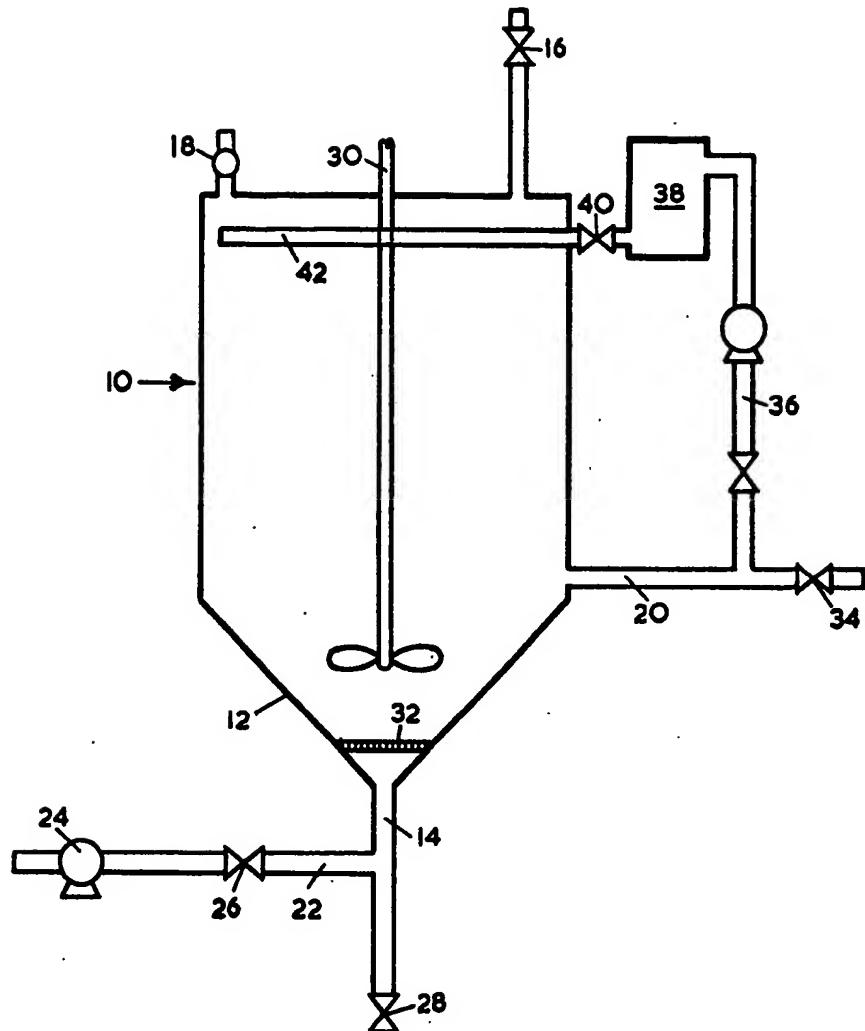


FIG. I

1,360,797 COMPLETE SPECIFICATION

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SHEET 2

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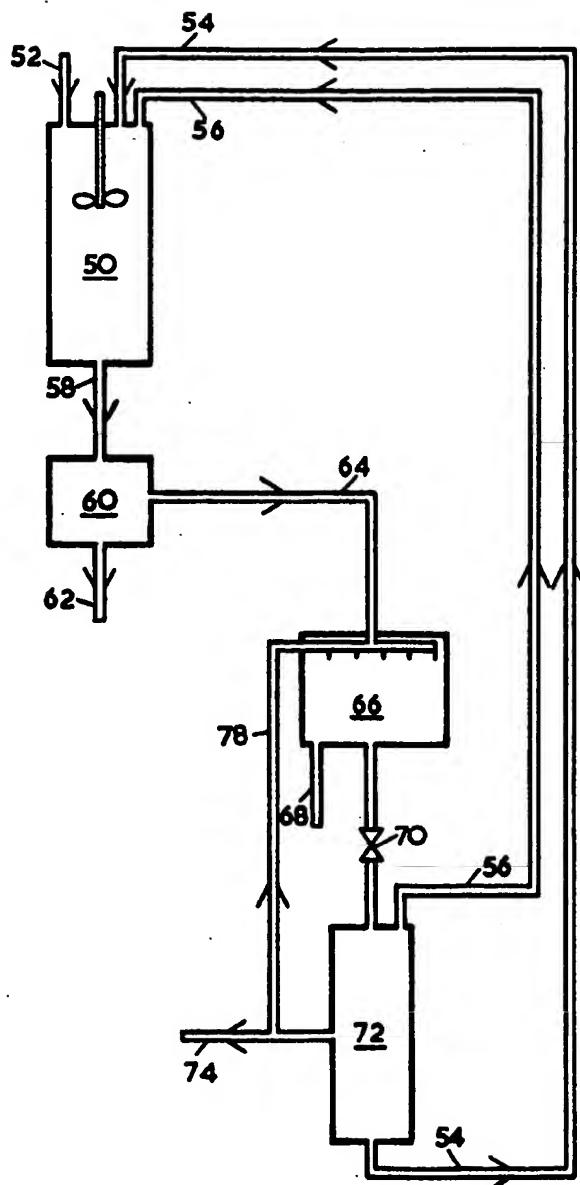


FIG.2